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TITLE: Glass composition for substrates - includes
oxide(s) of silicon,
aluminium, magnesium, calcium, potassium, zinc of
predetermined quantity

INVENTOR-NAME:

PRIORITY-DATA: 1996JP-0057953 (March 14, 1996)

PATENT-FAMILY:

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ABSTRACTED-PUB-NO: JP 09249430A

BASIC-ABSTRACT: The composition includes SiO₂ of 56-65
wt%, Al₂O₃ of 15- 23
wt%, MgO of 0-7 wt%, CaO of 0.-8 wt%, MgO+CaO of 4-15 wt%,
Na₂O of 0-9wt%, K₂O
of 0-11 wt%, Na₂O+K₂O of 8 to less than 12%, ZrO₂ of 0-2
wt%.

ADVANTAGE - Does not break since its heat resistance is
high. Realises
lightening of plasma display panel group plate glass,
accompanied by panel
expansion. Offers high productivity. Enables to be
produced by float glass
process.

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(22)Date of filing : 14.03.1996

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(54) GLASS COMPOSITION FOR SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a glass composition for substrate resistant to break, suitable to the production of a large-sized plasma display panel and having a high glass transition point by adopting a specific composition of glass.

SOLUTION: This glass composition for substrate is substantially composed of the following components in the indication of wt. %: SiO₂: 56-65, Al₂O₃: 15-23, MgO: 0-7, CaO: 0-8, MgO+CaO: 4-15, Na₂O: 0-9: K₂O: 0-11, Na₂O+K₂O: 8-less than 12, ZrO₂: 0-2. It is preferable that the composition has a degree of brittleness of less than 7,400m-1/2, a specific gravity of less than 2.6, a glass transition point of higher than 660°C and an average coefficient of thermal expansion in a range of 60×10-7-75×10-7/°C at 50-350°C.

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CLAIMS

[Claim(s)]

[Claim 1] By weight % display, substantially SiO₂ 56-65, aluminum 2O₃ 15 ** -23, MgO 0- 7 CaO 0- 8 MgO+CaO 4-15 and Na₂ O 0- 9 and K₂ O 0-11, and Na₂ O+K₂ O Eight to less than 12, and ZrO₂ 0- 2 -- a shell -- glass constituent for substrates

[Claim 2] The glass constituent for the substrates of the claim 1 whose brittleness index value is 1/2 or less [7400m -].

[Claim 3] The glass constituent for the substrates of the claims 1 or 2 whose specific gravity is less than 2.6.

[Claim 4] The glass constituent for the substrates of the claims 1, 2, or 3 in the range whose 50-350-degree C average coefficient of thermal expansion is 60×10^{-7} - 75×10^{-7} /degree C.

[Claim 5] The glass constituent for the substrates of the claims 1, 2, 3, or 4 whose glass transition points are 660 degrees C or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the glass constituent for substrates useful as a flat display, especially substrate glass for plasma display panels (PDP).

[0002]

[Description of the Prior Art] Generally, after PDP calcinates a metal electrode, an insulating paste, a rib paste, etc. by the about 550-600-degree C maximum temperature on substrate glass, it is manufactured by carrying out the frit seal of the circumference to an opposite board. Conventionally, generally the soda lime glass widely used as the object for construction or an object for automobiles as substrate glass for it has been used.

[0003] However, since substrate glass would deform or contract and a size would change remarkably if heat treatment is received by the above-mentioned maximum temperature, since it is 530-560 degrees C, the glass transition point of a soda lime glass had the technical problem that it was hard to realize electrode alignment with an opposite board with a sufficient precision. When manufacturing especially using the firing furnace of continuous system like the high belt furnace of productivity, the temperature gradient stuck by the nose of cam and the back end of a glass plate during baking, and there was a problem that a glass plate caused a dimensional change unsymmetrical forward and backward. When such a problem becomes the large-sized thing [as / whose size of a panel is 40 inches], it becomes more remarkable and heat-resistant higher substrate glass is needed.

[0004] In order to solve heat deformation of this glass substrate or the problem of a thermal contraction, glass with a high strain point [a soda lime glass, near, a glass transition point, and a strain point] coefficient of thermal expansion is known (JP,3-40933,A, JP,7-257937,A). Since it will be hard to cause a dimensional change unsymmetrical before and after becoming a problem by the soda lime glass even if it heat-treats PDP manufacture by the firing furnace of continuous system if such glass is used, a panel can be calcinated in a high precision.

[0005]

[Problem(s) to be Solved by the Invention] However, the handling by the manufacturing process is becoming still more difficult by enlargement of PDP in recent years. In order that especially a large-sized substrate may receive big bending stress in many cases with a self-weight, slight existence of a blemish leads to the crack in a manufacturing process. Moreover, as for each already proposed composition, specific gravity is 2.6 or more and lightweight-ization of a member also has the problem of being difficult.

[0006] the purpose of this invention solves the above-mentioned fault, cannot break easily, and is large-sized -- it is in offering the glass constituent for substrates which has a high glass transition point so that it may be suitable for manufacture of PDP

[0007]

[Means for Solving the Problem] Substantially this invention by weight % display SiO₂ 56-65, aluminum 2O₃ 15 ** - 23, MgO 0- 7 CaO 0- 8 MgO+CaO 4-15 and Na₂ O 0- 9 and K₂ O 0-11, and Na₂ O+K₂ O Eight to less than 12, and ZrO₂ 0- 2 -- a shell -- it is a glass constituent for substrates

[0008]

[Embodiments of the Invention] The reason for limitation of composition by this invention is as follows.

SiO₂ : There is a possibility that the thermal resistance of glass may become bad and the brittleness of glass may increase by the component which forms the frame of glass under at 56 % of the weight (it is only indicated as % below). On the other hand, by **, a coefficient of thermal expansion falls 65%. SiO₂ 58 - 63% of range is more desirable.

[0009] aluminum 2O₃ : Although it is effective in getting a glass transition point and raising thermal resistance, there

are few these effects at 15% or less. On the other hand, by **, the dissolution nature of glass falls 23%. aluminum 2O3 17 - 20% of range is more desirable among the above-mentioned range.

[0010] MgO: Although it is not an indispensable component, lower the viscosity at the time of the dissolution of glass, since there is an operation which promotes the dissolution, make it contain, and get. However, there is an inclination for the coefficient of thermal expansion and brittleness of glass to become large too much by ** 7%, and devitrification temperature becomes high. 1 - 5% of range of MgO is more desirable among the above-mentioned range.

[0011] CaO: Although it is not an indispensable component, lower the viscosity in the dissolution temperature of glass, since there is an effect which promotes the dissolution, make it contain, and get. However, there is an inclination for the coefficient of thermal expansion and brittleness of glass to become large too much by ** 8%, and devitrification temperature becomes high. 1 - 6% of range of CaO is more desirable among the above-mentioned range.

[0012] MgO+CaO: Lower the viscosity in the dissolution temperature of glass, and in order to make it easy to melt, contain at least one side 4% or more by ****. On the other hand, there is an inclination for the coefficient of thermal expansion and brittleness of glass to become large too much by ** 15% by ****, and devitrification temperature becomes high. 8 - 13% of range is more desirable among the above-mentioned range.

[0013] Na2 O: Although it is not an indispensable component, lower the viscosity at the time of the dissolution of glass, since there is an operation which promotes the dissolution, make it contain, and get. However, since a coefficient of thermal expansion becomes large too much by ** 9%, and the chemical durability of glass deteriorates and electric resistance becomes small, there is a possibility that the life of the electrode of PDP may become short. Na2 O has 1 - 7% of more desirable range among the above-mentioned range.

[0014] K2 O: Although it is not an indispensable component, lower the viscosity at the time of the dissolution of glass, since there is an operation which promotes the dissolution, make it contain, and get. However, by **, a coefficient of thermal expansion becomes large too much 11%, and there is an inclination for the chemical durability of glass to ****. K2 O has 2 - 9% of more desirable range among the above-mentioned range.

[0015] Na2 O+K2 O: Lower the viscosity in the dissolution temperature of glass, and in order to make it easy to melt, contain at least one side 8% or more by ****. On the other hand, when it becomes 12% or more by ****, there is an inclination for the coefficient of thermal expansion of glass to become large too much, and chemical durability falls and there is a possibility that electric resistance may become small. Less than 9 - 12% of range is more desirable among the above-mentioned range.

[0016] ZrO2 : Although it is not indispensable in order to get the glass transition point of glass, it is made to contain and gets. However, there is a possibility of bringing about increase of the brittleness of glass by ** 2%. At this viewpoint, it is ZrO2. Considering as less than 0.5% is desirable.

[0017] SO3 besides the above component, As 2O3, and Sb 2O3 etc. -- a clarifier, Fe 2O3, NiO, CoO and TiO2, Se, and CeO2 etc. -- a coloring agent etc. can be used suitably Moreover, in order to acquire the same effect as CaO and MgO, SrO, BaO, and ZnO can be added. Since increase [ZnO / SrO and] / of 2% or less and the brittleness specifically according / BaO / to addition respectively is large, it can add 2% or less by **** of SrO, BaO, and ZnO 1% or less.

[0018] furthermore, in order to acquire the same effect as Na2 O and K2 O, Li2 O can be added 1% or less However, too much Li2 O addition has a possibility of bringing about the fall of a glass transition point. Furthermore, it is B-2 O3 in order to improve solubility. It can add. However, since too much addition reduces a coefficient of thermal expansion, considering as less than 1.5% is desirable.

[0019] Moreover, as for the glass constituent for substrates of this invention, it is desirable that specific gravity is less than 2.6. It is 2.5 or less most preferably 2.55 or less.

[0020] Typically, since the glass constituent for substrates of this invention has a 50-350-degree C average coefficient of thermal expansion in the range which is 60×10^{-7} - 75×10^{-7} /degree C, it can assemble PDP using the frit material for alumina-ceramics substrates.

[0021] Moreover, as for the glass transition point of the glass constituent for substrates of this invention, it is desirable that it is 660 degrees C or more. It is more desirable that a glass transition point is 690 degrees C or more in the viewpoint of making the few display of distortion easier to manufacture.

[0022] As for especially the glass by this invention, it is desirable that a brittleness index value is 1/2 or less [7400m -], and it is 1/2 or less [7300m -] more preferably.

[0023] In addition, in this invention, the brittleness index value B proposed by loans as a brittleness index value of glass is used (B. R.Lawn and D.B.Marshall, J.Am.Ceram.Soc., and 62[7-8]347-350 (1979)). Here, the brittleness index value B is Vickers hardness number HV of material. Fracture toughness value KC A shell formula (1) defines.

[0024]

[Equation 1]

$$B = H_v / K_C \quad (1)$$

[0025] The glass of this invention is suitable as a substrate for plasma displays. As for the spectral transmittance, it is desirable that it is 85% or more, respectively in 425-475nm, 510-560nm, and 600-650nm. It is because luminescence in these wavelength ranges can use for a display efficiently.

[0026] The glass of this invention can be manufactured, for example by the following methods. Usually, the raw material of each component used is prepared so that it may become a target system, this is continuously supplied to a fusion furnace, and it heats and fuses at 1500-1650 degrees C. This melting glass is fabricated to predetermined board thickness by the float glass process, and is cut after annealing.

[0027]

[Example] The raw material of each component was prepared so that it might become a target system, and using the platinum crucible, at the temperature of 1550-1650 degrees C, it heated for 4 hours and melted. In the dissolution, the platinum stirrer was inserted, it agitated for 2 hours, and homogenizing of glass was performed. Subsequently, it was begun to pour dissolution glass and cooled slowly after fabricating to a tabular.

[0028] In this way, the specific gravity of the obtained glass, the average coefficient of thermal expansion α , the glass transition point T_g , and the brittleness index value B were measured by the following method, and were shown in Table 1 - 3 with glass composition.

[0029] Among these, Example 15 - Example 20 are examples of comparison, and Example 15 is [the example of a constituent given in JP,3-40933,A, Example 17 - Example 20 of the example of a soda lime glass and Example 16] examples of a constituent given in JP,7-257937,A. The measuring method of each property is described below.

[0030] Specific gravity: It is based on the Archimedes method.

Average coefficient of thermal expansion α (unit : $\times 10^{-7}/\text{degree C}$): Carrying out a temperature up by part for 5-degree-C/by making quartz glass into a reference sample using a differential thermal-expansion meter, the expansion curve to the point surrendering [a room temperature -] was measured, and the 50-350-degree C average coefficient of thermal expansion was read and recorded.

Glass transition point T_g : (unit : degree C) The tangent was drawn before and behind the folding point of the beginning of the coefficient-of-thermal-expansion curve at the time of coefficient-of-thermal-expansion measurement, and the temperature equivalent to the intersection was recorded as a glass transition point.

Brittleness index value B (unit : $\text{m}^{-1/2}$): The big problem at the time of applying the index of brittleness to glass is the fracture toughness value K_C . It is hard to evaluate correctly. However, as a result of examining some technique, these people have found out that brittleness can be quantitatively evaluated from the relation between the size of the marks of the indenter which remains in a glass front face, and the length of the crack generated from the four corners of marks, when the Vickers indenter is pushed in.

[0031] The relation is defined by the formula (2). Here, P is the pushing load of the Vickers indenter and a and c are the length (overall length of two symmetrical cracks containing the marks of an indenter) of the crack generated from the diagonal length and four corners of the Vickers indentation, respectively. The brittleness index value was evaluated using the size and formula (2) of the Vickers indentation which were driven into the front face of various glass.

[0032]

[Equation 2]

$$c/a = 0.0056 B^{2/3} P^{1/6} \quad (2)$$

[0033] A brittleness index value is $1/2$ or less [$7400\text{m}^{-1/2}$], and the glass by the example of this invention has little fear of the crack in a manufacturing process etc. so that more clearly than Table 1 - 3.

[0034] An average coefficient of thermal expansion is in the range of 60×10^{-7} - $75 \times 10^{-7}/\text{degree C}$, and can assemble PDP using the frit material for alumina-ceramics substrates. moreover, each glass transition point is 660 degrees C or more, and is large-sized -- there is no problem of glass deforming or contracting in manufacture of PDP Moreover, specific gravity is less than 2.6 and lightweight-izing at the time of using as a substrate for flat panels is easy.

[0035] On the other hand, since a glass transition point is 550 degrees C, Example 15 has a possibility that deformation and contraction of the glass in a PDP manufacturing process may pose a problem. The brittleness index value is over - $1/2$ $7400\text{m}^{-1/2}$, and Examples 16-20 tend to produce a crack in manufacture process etc. Moreover, each specific gravity of glass is 2.6 or more, and lightweight-izing of a member is difficult.

[0036]

[Table 1]

	1	2	3	4	5	6	7	8
SiO ₂ (重量%)	64.3	61.1	56.6	63.5	59.2	64.4	61.5	57.9
Al ₂ O ₃	16.7	16.5	22.6	18.8	17.5	19.1	16.6	18.4
MgO	3.8	4.6	4.2	0.0	6.9	4.8	4.4	3.9
CaO	5.7	6.9	6.3	7.1	6.6	0.0	7.0	7.2
SrO	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0
BaO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9
Na ₂ O	3.7	3.6	4.1	4.2	3.9	4.7	3.9	0.9
K ₂ O	5.7	6.2	6.2	6.4	5.9	7.1	5.9	10.8
ZrO ₂	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0
比重	2.47	2.51	2.51	2.45	2.52	2.41	2.50	2.51
α ($\times 10^{-7}/^{\circ}\text{C}$)	64	66	63	69	70	66	68	72
T _g ($^{\circ}\text{C}$)	716	752	724	736	705	746	707	729
B ($\text{m}^{-1/2}$)	6900	7300	7100	6800	7200	6800	7000	7100

[0037]

[Table 2]

	9	10	11	12	13	14
SiO ₂ (重量%)	59.1	60.1	61.3	61.6	59.6	57.9
Al ₂ O ₃	17.8	19.8	18.2	18.3	17.8	17.2
MgO	4.4	4.5	4.5	4.6	4.4	6.7
CaO	7.9	6.7	6.8	6.9	6.7	7.7
Na ₂ O	4.3	2.4	6.1	8.7	0.0	4.2
K ₂ O	6.5	6.6	3.1	0.0	11.0	6.4
ZrO ₂	0.0	0.0	0.0	0.0	0.5	0.0
比重	2.51	2.50	2.50	2.50	2.48	2.53
α ($\times 10^{-7}/^{\circ}\text{C}$)	73	62	67	66	66	75
T _g ($^{\circ}\text{C}$)	702	730	695	690	749	702
B ($\text{m}^{-1/2}$)	7100	7000	7100	7100	7000	7200

[0038]

[Table 3]

	1 5	1 6	1 7	1 8	1 9	2 0
S i O ₂ (重量%)	72.5	58.0	57.4	57.4	58.6	58.0
A l ₂ O ₃	1.0	10.0	12.1	12.1	14.2	12.5
M g O	2.5	4.0	3.0	3.0	2.0	2.0
C a O	9.5	9.0	5.9	7.9	5.1	5.0
S r O	0.0	3.8	1.0	1.0	2.0	2.0
B a O	0.0	3.0	4.0	4.0	3.0	6.0
Z n O	0.0	0.0	2.0	0.0	0.0	0.0
N a ₂ O	14.0	4.0	4.2	4.2	6.0	4.0
K ₂ O	0.5	6.0	8.2	8.2	6.1	8.0
Z r O ₂	0.0	2.0	2.2	2.2	3.0	2.5
S O ₃	0.0	0.2	0.0	0.0	0.0	0.0
比重	2.49	2.65	2.63	2.62	2.60	2.63
α ($\times 10^{-7} / ^\circ\text{C}$)	87	79	81	84	81	81
T _g ($^\circ\text{C}$)	550	645	655	646	654	652
B ($\text{m}^{-1/2}$)	7100	7600	7600	7500	7500	7600

[0039]

[Effect of the Invention] The glass by this invention cannot break easily, and since thermal resistance is high, the substrate for plasma displays etc. is suitable for it for the use which requires this property. Moreover, since specific gravity is small, lightweight-ization of the PDP substrate glass accompanying enlargement of a panel is realizable. Moreover, since the coefficient of thermal expansion is smaller than soda lime glass, it is hard to carry out a heat crack at the heat treatment process under manufacture, and productivity is high. Furthermore, the glass by this invention also fits production by the float glass process.

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(54) 【発明の名称】 基板用のガラス組成物

(57) 【要約】

【課題】割れにくく、耐熱性の高い、プラズマディスプレイ用基板等に好適なガラス組成物を得る。

【解決手段】重量%表示で実質的に、SiO₂ : 56~65、Al₂O₃ : 15超~23、MgO : 0~7、CaO : 0~8、MgO+CaO : 4~15、Na₂O : 0~9、K₂O : 0~11、Na₂O+K₂O : 8~12、ZrO₂ : 0~2からなる。

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【特許請求の範囲】

【請求項1】重量%表示で実質的に、

SiO ₂	56～65、
Al ₂ O ₃	15超～23、
MgO	0～7、
CaO	0～8、
MgO+CaO	4～15、
Na ₂ O	0～9、
K ₂ O	0～11、
Na ₂ O+K ₂ O	8～12未満、
ZrO ₂	0～2、

からなる基板用のガラス組成物。

【請求項2】脆さ指標値が $7400\text{ m}^{-1/2}$ 以下である請求項1の基板用のガラス組成物。

【請求項3】比重が2.6未満である請求項1または2の基板用のガラス組成物。

【請求項4】50～350℃の平均熱膨張係数が $60\times 10^{-7}\sim 75\times 10^{-7}/^{\circ}\text{C}$ の範囲にある請求項1、2または3の基板用のガラス組成物。

【請求項5】ガラス転移点が660℃以上である請求項1、2、3または4の基板用のガラス組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、フラットディスプレイ、特にプラズマディスプレイパネル(PDP)用基板ガラスとして有益な基板用ガラス組成物に関する。

【0002】

【従来の技術】PDPは一般的に、基板ガラス上に金属電極、絶縁ペースト、リブペースト等を550～600℃程度の最高温度で焼成した後、対向板と周囲をフリットシールすることにより製造される。従来、このための基板ガラスとして建築用または自動車用として広く用いられるソーダ石灰ガラスが一般的に用いられてきた。

【0003】しかし、ソーダ石灰ガラスのガラス転移点は530～560℃であるため、上記の最高温度で熱処理を受けると基板ガラスが変形または収縮し、寸法が著しく変化するため、対向板との電極位置合わせを精度良く実現しがたいという課題があった。特に、生産性の高いベルト炉のような連続式の焼成炉を使用して製造する場合、焼成中にガラス板の先端と後端で温度差がつき、ガラス板が前後に非対称な寸法変化を起こすという問題があった。このような問題は、パネルの大きさが例えば40インチのような大型なものになるとより顕著になり、耐熱性のより高い基板ガラスが必要となる。

【0004】このガラス基板の熱変形または熱収縮の問題を解決するため、熱膨張係数がソーダ石灰ガラスと近く、ガラス転移点、歪点が高いガラスが知られている(特開平3-40933、特開平7-257937)。このようなガラスを用いると、連続式の焼成炉でPDP製造の熱処理を行っても、ソーダ石灰ガラスで問題とな

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るような前後に非対称な寸法変化を起こしにくいいため、高い精度でパネルを焼成できる。

【0005】

【発明が解決しようとする課題】しかし、近年のPDPの大型化により、製造工程でのハンドリングがますます困難になってきている。特に、大型基板は自重により大きな曲げ応力を受けることが多いため、わずかな傷の存在が、製造工程での割れにつながる。また、すでに提案されている組成は、いずれも比重が2.6以上であり、部材の軽量化が困難であるという問題もある。

【0006】本発明の目的は、上記欠点を解決し、割れにくく、大型PDPの製造に適するように高いガラス転移点を有する基板用ガラス組成物を提供することにある。

【0007】

【課題を解決するための手段】本発明は、重量%表示で実質的に、

SiO ₂	56～65、
Al ₂ O ₃	15超～23、
MgO	0～7、
CaO	0～8、
MgO+CaO	4～15、
Na ₂ O	0～9、
K ₂ O	0～11、
Na ₂ O+K ₂ O	8～12未満、
ZrO ₂	0～2、

からなる基板用のガラス組成物である。

【0008】

【発明の実施の形態】本発明による組成の限定理由は以下の通りである。

SiO₂:ガラスの骨格を形成する成分で、56重量%(以下単に%と記載する)未満では、ガラスの耐熱性が悪くなり、またガラスの脆さが増大するおそれがある。他方、65%超では熱膨張係数が低下する。SiO₂は、58～63%の範囲がより好ましい。【0009】Al₂O₃:ガラス転移点を上げ、耐熱性を向上させる効果があるが、15%以下ではこの効果が少ない。他方、23%超ではガラスの溶解性が低下する。Al₂O₃は、上記範囲中17～20%の範囲がより好ましい。

【0010】MgO:必須成分ではないが、ガラスの溶解時の粘性を下げ、溶解を促進する作用があるので含有させうる。しかし、7%超ではガラスの熱膨張係数や脆さが大きくなりすぎる傾向があり、かつ失透温度が高くなる。MgOは、上記範囲中1～5%の範囲がより好ましい。

【0011】CaO:必須成分ではないが、ガラスの溶解温度での粘性を下げ、溶解を促進する効果があるので含有させうる。しかし、8%超ではガラスの熱膨張係数や脆さが大きくなりすぎる傾向があり、かつ失透温度が

高くなる。CaOは、上記範囲中1～6%の範囲がより好ましい。

【0012】MgO+CaO：ガラスの熔解温度での粘性を下げ、熔解しやすくするため、少なくとも一方を含量で4%以上含有する。他方、含量で15%超ではガラスの熱膨張係数や脆さが大きくなりすぎる傾向があり、かつ失透温度が高くなる。上記範囲中8～13%の範囲がより好ましい。

【0013】Na₂O：必須成分ではないが、ガラスの熔解時の粘性を下げ、熔解を促進する作用があるので含有させうる。しかし、9%超では熱膨張係数が大きくなりすぎ、ガラスの化学的耐久性が劣化し、また、電気抵抗が小さくなるため、PDPの電極の寿命が短くなるおそれがある。Na₂Oは、上記範囲中1～7%の範囲がより好ましい。

【0014】K₂O：必須成分ではないが、ガラスの熔解時の粘性を下げ、熔解を促進する作用があるので含有させうる。しかし、11%超では熱膨張係数が大きくなりすぎ、ガラスの化学的耐久性が低下する傾向がある。K₂Oは、上記範囲中2～9%の範囲がより好ましい。

【0015】Na₂O+K₂O：ガラスの熔解温度での粘性を下げ、熔解しやすくするため、少なくとも一方を含量で8%以上含有する。他方、含量で12%以上になるとガラスの熱膨張係数が大きくなりすぎる傾向があり、かつ化学的耐久性が低下し、電気抵抗が小さくなるおそれがある。上記範囲中9～12%未満の範囲がより好ましい。

【0016】ZrO₂：ガラスのガラス転移点を上げるために、必須ではないが、含有させうる。しかし、2%超ではガラスの脆さの増大をもたらすおそれがある。この観点では、ZrO₂は0.5%未満とされることが好ましい。

【0017】以上の成分の他、SO₃、As₂O₃、Sb₂O₃等の澄清剤、Fe₂O₃、NiO、CoO、TiO₂、Se、CeO₂等の着色剤等を適宜使用できる。また、CaO、MgOと同様の効果を得るために、SrO、BaO、ZnOを添加できる。具体的には、SrOおよびZnOはそれぞれ2%以下、BaOは添加による脆さの増大が大きいので1%以下、SrO、BaO、ZnOの含量で2%以下添加できる。

【0018】さらに、Na₂O、K₂Oと同様の効果を得るために、Li₂Oを1%以下添加できる。ただし過度のLi₂O添加は、ガラス転移点の低下をもたらすおそれがある。さらに、溶解性を向上するためにB₂O₃を添加できる。ただし、過度の添加は、熱膨張係数を低下させるので1.5%未満とすることが好ましい。

【0019】また、本発明の基板用ガラス組成物は、比重が2.6未満であることが好ましい。より好ましくは、2.55以下、もっとも好ましくは2.5以下であ

る。

【0020】本発明の基板用ガラス組成物は、典型的には、50～350℃の平均熱膨張係数が $60 \times 10^{-7} \sim 75 \times 10^{-7} / ^\circ\text{C}$ の範囲にあるので、アルミナセラミックス基板用のフリット材料を用いて、PDPを組み立てることができる。

【0021】また、本発明の基板用ガラス組成物のガラス転移点は660℃以上であることが好ましい。より歪みの少ないディスプレイを製造しやすくするという観点では、ガラス転移点が690℃以上であることがより好ましい。

【0022】特に、本発明によるガラスは脆さ指標値が $7400 \text{ m}^{-1/2}$ 以下であることが好ましく、より好ましくは、 $7300 \text{ m}^{-1/2}$ 以下である。

【0023】なお、本発明において、ガラスの脆さ指標値としてはローンらによって提案された脆さ指標値Bを使用する(B.R.Lawn and D.B.Marshall, J. Am. Ceram. Soc., 62[7-8]347-350(1979))。ここで、脆さ指標値Bは材料のビッカース硬さHvと破壊靱性値K_{IC}から式(1)により定義される。

【0024】

【数1】

$$B = H_v / K_{IC} \quad (1)$$

【0025】本発明のガラスは、プラズマディスプレイ用基板として好適である。その分光透過率は425～475nm、510～560nm、600～650nmの範囲でそれぞれ85%以上となっていることが好ましい。これらの波長範囲での発光が効率的に表示に利用できるからである。

【0026】本発明のガラスは、例えば次のような方法で製造できる。通常使用される各成分の原料を目標組成になるように調合し、これを熔解炉に連続的に投入し、1500～1650℃に加熱して溶融する。この溶融ガラスをフロート法により所定の板厚に成形し、徐冷後切断する。

【0027】

【実施例】各成分の原料を目標組成になるように調合し、白金坩堝を用いて、1550～1650℃の温度で4時間加熱し熔解した。熔解にあたっては、白金スターラを挿入し2時間攪拌しガラスの均質化を行った。次いで熔解ガラスを流し出し、板状に成形後徐冷した。

【0028】こうして得られたガラスの比重、平均熱膨張係数 α 、ガラス転移点T_g、脆さ指標値Bを下記の方法で測定し、表1～表3にガラス組成とともに示した。

【0029】このうち、例15～例20は比較例であり、例15はソーダ石灰ガラスの例、例16は特開平3-40933記載の組成物の例、例17～例20は特開平7-257937記載の組成物の例である。以下に各特性の測定方法を述べる。

【0030】比重：アルキメデス法による。

平均熱膨張係数 α (単位: $\times 10^{-7}/^{\circ}\text{C}$): 示差熱膨張計を用い、石英ガラスを参照試料として $5^{\circ}\text{C}/\text{分}$ で昇温しながら、室温～屈伏点までの膨張曲線を測定し、 $50\sim 350^{\circ}\text{C}$ の平均熱膨張係数を読み取り、記録した。

ガラス転移点 T_g (単位: $^{\circ}\text{C}$): 熱膨張係数測定時の熱膨張係数曲線の最初の屈曲点の前後で接線を引き、その交点に相当する温度をガラス転移点として記録した。

脆さ指標値 B (単位: $\text{m}^{-1/2}$): 脆さの指標をガラスに適用する際の大きな問題は破壊靱性値 K_{IC} が正確に評価しにくいことである。しかしながら、本出願人は、いくつかの手法を検討した結果、ビッカース圧子を押し込んだときにガラス表面に残る圧子の痕の大きさと痕の四隅から発生するクラックの長さとの関係から脆さを定量的に評価できることを見いだしている。

【0031】その関係は式(2)により定義される。ここで、 P はビッカース圧子の押し込み荷重であり、 a 、 c はそれぞれ、ビッカース圧痕の対角長および四隅から発生するクラックの長さ(圧子の痕を含む対称な2つのクラックの全長)である。各種ガラスの表面に打ち込んだビッカース圧痕の寸法と式(2)を用いて、脆さ指標値を評価した。

【0032】

*【数2】

$$c/a = 0.0056 B^{2/3} P^{1/6} \quad (2)$$

【0033】表1～表3より明らかなように、本発明の実施例によるガラスは、脆さ指標値が $7400 \text{m}^{-1/2}$ 以下であり、製造工程などにおける割れのおそれが少ない。

【0034】平均熱膨張係数は、 $60 \times 10^{-7} \sim 75 \times 10^{-7}/^{\circ}\text{C}$ の範囲にあり、アルミナセラミックス基板用のフリット材料を用いて、PDPを組み立てうる。また、ガラス転移点はいずれも 660°C 以上であり、大型PDPの製造においてガラスが変形したり収縮したりする等の問題がない。また、比重が2.6未満であり、フラットパネル用基板として用いた場合の軽量化が容易である。

【0035】一方、例15はガラス転移点が 550°C であるため、PDP製造工程でのガラスの変形や収縮が問題となるおそれがある。例16～20は脆さ指標値が $7400 \text{m}^{-1/2}$ を超えており、製造過程などで割れを生じやすい。また、ガラスの比重がいずれも2.6以上で、部材の軽量化が困難である。

【0036】

*【表1】

	1	2	3	4	5	6	7	8
SiO_2 (重量%)	64.3	61.1	56.6	63.5	59.2	64.4	61.5	57.9
Al_2O_3	16.7	16.5	22.6	18.8	17.5	19.1	16.6	18.4
MgO	3.8	4.6	4.2	0.0	6.9	4.8	4.4	3.9
CaO	5.7	6.9	6.3	7.1	6.6	0.0	7.0	7.2
SrO	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0
BaO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9
Na_2O	3.7	3.6	4.1	4.2	3.9	4.7	3.9	0.9
K_2O	5.7	6.2	6.2	6.4	5.9	7.1	5.9	10.8
ZrO_2	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0
比重	2.47	2.51	2.51	2.45	2.52	2.41	2.50	2.51
α ($\times 10^{-7}/^{\circ}\text{C}$)	64	66	63	69	70	66	68	72
T_g ($^{\circ}\text{C}$)	716	752	724	736	705	746	707	729
B ($\text{m}^{-1/2}$)	6900	7300	7100	6800	7200	6800	7000	7100

【0037】

※ ※【表2】

	9	10	11	12	13	14
SiO ₂ (重量%)	59.1	60.1	61.3	61.6	59.6	57.9
Al ₂ O ₃	17.8	19.8	18.2	18.3	17.8	17.2
MgO	4.4	4.5	4.5	4.6	4.4	6.7
CaO	7.9	6.7	6.8	6.9	6.7	7.7
Na ₂ O	4.3	2.4	6.1	8.7	0.0	4.2
K ₂ O	6.5	6.6	3.1	0.0	11.0	6.4
ZrO ₂	0.0	0.0	0.0	0.0	0.5	0.0
比重	2.51	2.50	2.50	2.50	2.48	2.53
α ($\times 10^{-7}/^{\circ}\text{C}$)	73	62	67	66	66	75
T _g ($^{\circ}\text{C}$)	702	730	695	690	749	702
B ($\text{m}^{-1}/^{\circ}$)	7100	7000	7100	7100	7000	7200

【0038】

* * 【表3】

	15	16	17	18	19	20
SiO ₂ (重量%)	72.5	58.0	57.4	57.4	58.6	58.0
Al ₂ O ₃	1.0	10.0	12.1	12.1	14.2	12.5
MgO	2.5	4.0	3.0	3.0	2.0	2.0
CaO	9.5	9.0	5.9	7.9	5.1	5.0
SrO	0.0	3.8	1.0	1.0	2.0	2.0
BaO	0.0	3.0	4.0	4.0	3.0	6.0
ZnO	0.0	0.0	2.0	0.0	0.0	0.0
Na ₂ O	14.0	4.0	4.2	4.2	6.0	4.0
K ₂ O	0.5	6.0	8.2	8.2	6.1	8.0
ZrO ₂	0.0	2.0	2.2	2.2	3.0	2.5
SO ₃	0.0	0.2	0.0	0.0	0.0	0.0
比重	2.49	2.65	2.63	2.62	2.60	2.63
α ($\times 10^{-7}/^{\circ}\text{C}$)	87	79	81	84	81	81
T _g ($^{\circ}\text{C}$)	550	645	655	646	654	652
B ($\text{m}^{-1}/^{\circ}$)	7100	7600	7600	7500	7500	7600

【0039】

【発明の効果】本発明によるガラスは、割れにくく、耐熱性が高いため、プラズマディスプレイ用基板等、かかる特性を要求する用途に好適である。また、比重が小さいため、パネルの大型化にともなうPDP基板ガラスの※

※軽量化を実現できる。また、熱膨張係数がソーダライムガラスより小さいため、製造中の熱処理工程で熱割れしにくく、生産性が高い。さらに本発明によるガラスは、フロート法による生産にも適する。